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LETTER TO THE EDITOR

Thomas–Fermi screening of exchange interactions**M S S Brooks**European Commission, Joint Research Centre, Institute for Transuranium Elements,
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Abstract

Exchange integrals for a screened Coulomb interaction of the Yukawa form with the Thomas–Fermi wave vector expressed in terms of the total electron density are calculated for transition metal, rare-earth and actinide atoms. The calculated exchange interactions are in remarkable agreement with those obtained from the local spin-density approximation.

Exchange interactions in the homogeneous electron gas have been studied both rigorously and extensively and some of the results have been incorporated in atomic and solid-state calculations via density functional theory [1], usually in the local spin-density approximation (LSDA) [2]. A good approximation to the LSDA spin-polarization energy of an atom, in terms of radial integrals and the partial spin moments, m_l , of all open shells, is [3, 4]

$$E_{SP}^{LSDA} = -\frac{1}{4} \sum_{l,l'} J_{ll'} m_l m_{l'} \quad (1)$$

where the LSDA atomic exchange integral matrices are given by

$$J_{ll'} = \frac{2}{3} \int r^2 \phi_l^2(r) \phi_{l'}^2(r) A[n(r)]/n(r) dr \quad (2)$$

and $A(r)$ is a function of the density which varies a little depending upon which version of LSDA is used [5].

An alternative derivation of the spin-polarization energy, which predated the LSDA, was due to Slater [6] and was based upon the Hartree–Fock approximation (HFA) with the orbitals for a given spin in the (lm) representation assumed to be uniformly populated with occupation numbers

$$n_{lm}^{\pm} = q_l^{\pm} / (2l + 1) \quad (3)$$

where q_l^{\pm} is the number of electrons with l -character and spin \pm . Then the HFA spin-polarization energy is

$$E_{SP}^{HFA} = -\frac{1}{4} \sum_{l,l'} V_{ll'} m_l m_{l'}. \quad (4)$$

Although equations (1) and (4) have the same quadratic form, the exchange integrals, $V_{ll'}$, are linear combinations of the radial Slater exchange integrals rather than functions of the electron density:

$$V_{ll'} = \sum_k \begin{pmatrix} l & l' & k \\ 0 & 0 & 0 \end{pmatrix}^2 G^k(ll'l') \quad (5)$$

where (\dots) is a Wigner $3j$ -symbol. In the sum over k in equation (5), $l + l' + k$ must be even; otherwise the $3j$ -symbol is zero. The approximation defined by equation (3) imposes spherical symmetry and isolates the isotropic exchange interactions. More general expressions for the spin-polarization energy have also been derived [7], particularly for the LDA + U approximation [8], but equation (5) is suitable for a comparison of the HFA and LSDA.

There is no contribution to E_{SP}^{HFA} from the spherical Coulomb integral, G^0 , between shells since

$$\begin{pmatrix} l & l' & 0 \\ 0 & 0 & 0 \end{pmatrix} = 0 \quad \text{for } l \neq l'.$$

However, within a shell,

$$\begin{pmatrix} l & l & 0 \\ 0 & 0 & 0 \end{pmatrix} = (2l + 1)^{-1/2}$$

and the contribution to V_{ll} is $G^0(lll)/(2l + 1)$. This contribution was omitted by Slater [6] even for intra-shell exchange and has since been the subject of some controversy since it is the self-exchange responsible for the self-interaction cancellation [9, 10], and is sometimes regarded as not a true exchange interaction [11]. Its origin is physically very simple. For non-integral occupation numbers an orbital is occupied by equal numbers of electrons (≤ 0.5) with spin up and spin down in the paramagnetic state, in which case the spin-up and spin-down electrons interact. In the spin-polarized state, with just the spin-up orbitals occupied, this self-interaction disappears and the energy gain appears as part of the spin-polarization energy.

Calculated exchange interactions based upon equation (5) are far too large since the Coulomb interaction is unscreened in the HFA. Applications of the HFA, such as the LDA + U approximation [8], are therefore plagued by the requirement to scale the HFA integrals in some manner which is frequently empirical [12] or by means of a supercell calculation [13]. A simple approximation for screening that may be incorporated in a self-consistent calculation is therefore desirable since the GW -approximation [14] is difficult to implement. Norman [15] used the simplest screened Coulomb interaction with a Yukawa form:

$$V(\mathbf{r}, \mathbf{r}') = \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad (6)$$

to calculate screened Slater integrals for Pr and U ions. Norman took the inverse screening length, κ , to be an adjustable parameter and found the value required to fit analysis of atomic spectroscopy experiments. In this letter we suggest an additional step—using Thomas–Fermi [16] screening which delivers a position-dependent value of κ directly in terms of the total density:

$$\kappa[n(r'')] = 2[3n(r'')/\pi]^{1/6} \quad (7)$$

where $r'' = (r + r')/2$. The screened interaction is then expanded in spherical functions:

$$V(\mathbf{r}, \mathbf{r}') = -\kappa \sum_l (2l + 1) j_l(i\kappa r_<) h_l^{(1)}(i\kappa r_>) P_l(\cos \theta) \quad (8)$$

where, as usual, $r_<$, $r_>$ refer to the lesser or greater of r , r' , j_l and $h_l^{(1)}$ are spherical Bessel and Hankel functions of imaginary argument. The screened radial Slater integrals are

$$G^k(l'l') = - \int \int r^2 r'^2 j_k(ikr_<) h_k^{(1)}(ikr_>) R_l(r) R_{l'}(r') R_l(r') R_{l'}(r) dr dr'. \quad (9)$$

Figure 1 shows the calculated exchange integrals, equations (2) and (5), for free atoms of the 3d series. The unscreened HFA integrals are far too large, primarily due to the unscreened G^0 -integrals. The strong screening of the G^0 -integrals plus the somewhat weaker screening of the higher-order integrals leads to values of the HFA exchange (labelled 'HF-scr') of the same order of magnitude as, but larger than, the values obtained from the LSDA. The screened G^0 -contribution to the exchange integrals is about half of the total. When it is removed, the Hartree–Fock ('HF-exch') and LSDA ('LSDA-exch') exchange integrals are almost identical. The calculated integrals for free atoms of the other transition metal series and the actinides (figure 2) follow the same pattern. When the G^0 -contribution is subtracted from the screened HFA ('HF-scr') contribution the LSDA result is recovered.

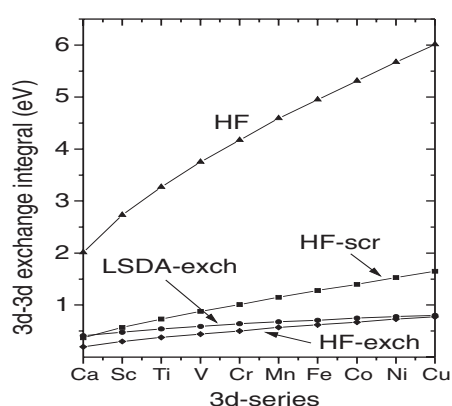


Figure 1. The exchange integrals for the 3d shell calculated from equations (2) and (5). 'HF' denotes unscreened Hartree–Fock integrals, 'HF-scr' denotes screened Hartree–Fock integrals (including the screened G^0 -contribution), whereas in 'HF-exch', G^0 is excluded. 'LSDA-exch' labels the LSDA exchange—or Stoner parameter.

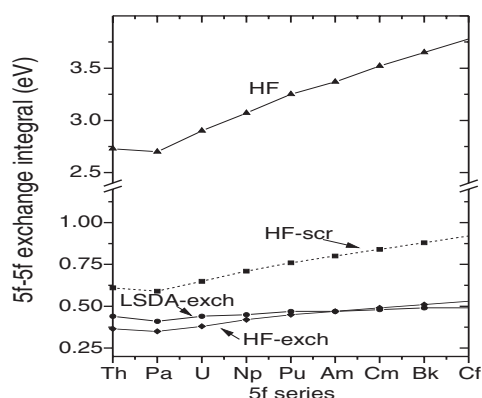


Figure 2. The exchange integrals for the 5f actinide shell calculated from equations (2) and (5). The labels are defined in the caption to figure 1.

In the rare-earth metals and their compounds the conduction electrons transmit the exchange interactions between local atomic moments. The local exchange interactions between rare-earth 4f and conduction electrons at the rare-earth sites may be calculated from equation (2) or equation (5). The LSDA exchange integrals are known to produce excellent results for exchange splitting of the conduction bands and conduction electron polarization induced by the 4f electrons. For example, the calculated conduction electron polarization of Gd metal is $0.65 \mu_B$ [17] compared with a measured $0.63 \mu_B$ [18] and for several series of rare-earth compounds the LSDA yields excellent results for the conduction electron moment [19].

Attempts have also been made to derive 4f–conduction electron exchange interactions from the HFA. Li *et al* [20] have derived the following expression for the isotropic exchange interaction between the 4f and other angular momentum states:

$$J_{4f-nl} = \frac{1}{\sqrt{7(2l+1)}} \left[\sum_k \langle f || C^{(k)} || l \rangle \begin{Bmatrix} 3 & 3 & 0 \\ l & l & k \end{Bmatrix}^2 G^k(4f, nl) \right] \quad (10)$$

where $\{\dots\}$ is a Wigner 6j-symbol. It is easy to show, by evaluating the reduced matrix element of the spherical tensor, $C^{(k)}$, and expanding the 6j-symbol, that J_{4f-nl} is identical to V_{3l} in equation (5). The problem that arises with this theory is that the calculated unscreened HFA exchange integrals are far too large, even though G^0 does not contribute to inter-shell exchange, especially for the most important 4f–5d exchange. The calculated 4f–5d and 4f–5p integrals for free atoms of Ce, Pr and Gd are listed in table 1. Most of the conduction electron spin in the rare-earth metals is carried by the 5d states; therefore the 4f–5d exchange integrals are critical. That the unscreened HFA 4f–5d exchange integral is far too large was used as an argument against using the HFA for the rare earths [19]. However, the screened integrals agree almost perfectly with the corresponding LSDA integrals. Use of the unscreened integrals led Li *et al* [20] to use unphysical averaging of the s, p and d exchange interactions to reduce the magnitude of the effective exchange—with screened exchange interactions this is no longer necessary.

Table 1. Calculated exchange integrals (in meV) for Ce, Pr and Gd. ‘Li *et al*’: taken from reference [20] for the $4f^x 5d^1 6s^1 6p^1$ configuration. The present calculations were made for the $4f^x 5d^2 6s^1 6p^0$ configuration and ‘HF’ refers to the unscreened HFA (equation (5)), ‘S-HF’ to the screened HFA (equation (5)) and ‘LSDA’ to the local spin-density approximation (equation (2)).

	Ce	Pr	Gd
4f–5d			
Li <i>et al</i>	230	221	189
HF	208	197	160
S-HF	112	108	93
LSDA	115	108	85
4f–6p			
Li <i>et al</i>	18	17	15
HF	20	20	17
S-HF	16	15	13
LSDA	20	18	14

The reason that the 4f–5d exchange integrals decrease across each series is the contraction of the 4f shell. The overlap between 4f and 5d densities occurs over a relatively small region of space corresponding to the outer part of the 4f density and the inner part of the 5d density. As the 4f shell contracts the region of overlap decreases.

Experience has shown that the LSDA integrals lead to splittings of energy bands and calculated magnetic moments that are in better agreement with measurements than if the

HFA is used [21]. The results of research on the magnetism of highly correlated electron systems, however, suggest that the LSDA runs into difficulties when the nodal properties of the wave functions become important to the exchange interactions [8]. Here we have shown that the simplest possible parameter-free approximation to screening—a variable Thomas–Fermi screening length—produces reasonable results for exchange integrals throughout the periodic table, suggesting that *ab initio* calculations of HFA exchange in solids are a practical possibility.

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